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Simultaneous measurement of integrated columns of NO_2, N_2O, NO and H_2O using ground-based solar infrared spectroradiometer

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Abstract : Ground based high resolution infrared absorption spectra recorded at National Physical Laboratory, New Delhi (28.7°N and 77.2°E) during 1992-93, have been analysed to determine the integrated columns of NO_2, N_2O, NO and H_2O. These measurements have also been used to study their seasonal dependence. An attempt has also been made to qualitatively correlate these measurements with available total ozone Dobson data under same conditions.

Keywords : NO_x, infrared absorption spectra, troposphere stratosphere

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1. Introduction

In view of the ozone depletion problem gaining momentum day by day, a study of role of catalytical species HO_x, NO_x and ClO_x rising to the stratosphere from the troposphere, has become important as these species are instrumental in ozone depletion [1,2]. It is therefore, of utmost importance to have simultaneous measurements of as many of these species as possible, to have a complete picture of the processes taking place in the stratosphere. These processes can not be understood properly, unless an extensive global data set is available. While in mid- and high-latitude locations, these data are available to some extent, at low latitude stations, these data are sparse. We have therefore, undertaken measurements of these parameters at a low latitude station New Delhi, by a reliable technique.

Different techniques have been used for the measurement of NO_x species [3–10]; infrared absorption spectroscopy is one among them. In this technique, atmospheric long

geometric path obtainable at large zenith angles, is a major advantage in increasing the sensitivity of measurements. Absence of instrumental pollution, possibility of simultaneous measurements of several species and high signal to noise ratio in ground based measurements are other advantages. The infrared solar spectra obtained from the ground, contain information on the chemical state of the atmosphere over the site at the time they were taken, since majority of the absorption features are of telluric origin. They are not specific species but contain information on all compounds with absorption features in the spectra. Thus the spectra can be re-examined at a later time as the features are identified or corrected for improved molecular spectral data.

In this paper, we report the simultaneous measurements of integrated columns of NO_2, N_2O, NO and H_2O using absorption features initially at 6.184, 8.560, 5.770 and 6.500 μm respectively, using solar infrared spectroradiometer during May, June and July 1992 and finally, using spectral lines of 6.232, 8.486, 5.415 and 6.500 μm respectively during November, December 1992 and January 1993. The absorption features at 6.232 μm, 8.486 μm, 5.415 μm of NO_2, N_2O and NO respectively have been used in previous studies of spectra obtained with aircraft born interferometer [11], and absorption features at 6.500 μm has been used in previous studies of spectra obtained from ground with solar infrared spectroradiometer [12]. It may be mentioned that an accurate quantitative determination of the trace constituents by this technique, depends on the selection of line parameters. The absorption lines should not be extremely weak besides being fairly distinct from the absorption features of the other atmospheric absorber. The Dobson data obtained from Indian Meteorological Department (IMD) for the same period and site is also utilised to study the variation trend of ozone with NO_x compounds and water vapour.

2. Theory

The intensity of the radiation of wavelength λ reaching the grating of infrared spectroradiometer after going through extinction process is expressed by Bouguer Lambert equation as follows :

$$I_\lambda = I_{0,\lambda} \exp[-m(\tau_\lambda)], \tag{1}$$

where $I_{0,\lambda}$ is the intensity of radiation of wavelength λ at the top of the atmosphere, m is the air mass in the optical path and is calculated as a function of zenith angle χ of the sun (m = sec χ) and τ_λ is the total optical thickness of the atmosphere in the vertical direction at the place of observation.

The optical thickness in turn, contains the contribution of Rayleigh molecular scattering, the scattering due to the presence of aerosol in the atmosphere and the absorption from the various gases present in the atmosphere. Thus, we have

$$I_\lambda = I_{0,\lambda} \exp\left[- m(\tau_{R,\lambda} + \tau_{\text{aer},\lambda} + \tau_{\text{abs},\lambda})\right] \tag{2}$$

where $\tau_{R,\lambda}$ = Rayleigh optical depth,

$\tau_{\text{aer},\lambda}$ = Aerosol optical depth.

$\tau_{\text{abs}\,\lambda}$ = Optical depth due to absorption by the various gases present in the atmosphere.

Since the molecule under study is the only chemical element that brings a significant contribution to the total mechanism of radiations in the atmosphere at the wavelengths λ_1 and λ_2, we can write

$$\tau_{\text{abs},\lambda_1} = \tau_{x,\lambda_1} \; ; \; \tau_{\text{abs},\lambda_2} = \tau_{x,\lambda_2}$$

where X represents any one of species NO_2, N_2O, NO or H_2O.

Therefore, eq. (2) becomes

$$I_{\lambda_1} = I_{0,\lambda_1} \exp\left[-m(\tau_{R,\lambda_1} + \tau_{\text{aer},\lambda_1} + \tau_{x,\lambda_1})\right], \tag{3}$$

$$I_{\lambda_2} = I_{0,\lambda_2} \exp\left[-m(\tau_{R,\lambda_2} + \tau_{\text{aer},\lambda_2} + \tau_{x,\lambda_2})\right]. \tag{4}$$

Wavelengths λ_1 and λ_2 being very near to each other and the centre of absorption band falling at $\lambda = \lambda_1$,

we have $$\tau_{R,\lambda_1} = \tau_{R,\lambda_2} \; ; \; \tau_{\text{aer},\lambda_1} = \tau_{\text{aer},\lambda_2}. \tag{5}$$

Taking into account eqs. (3)–(5), we have

$$I_{\lambda_1}/I_{\lambda_2} = \exp\left[-m(\tau_{x,\lambda_1} - \tau_{x,\lambda_2})\right]. \tag{6}$$

Presuming K_{x,λ_1} is the absorption coefficient at wavelength λ_1, we obtain

$$\tau_{x,\lambda_1} = W K_{x,\lambda_1}$$

and $$\tau_{x,\lambda_2} = W K_{x,\lambda_2},$$

where W is the integrated column of X. Therefore, eq. (6) becomes

$$I_{\lambda_1}/I_{\lambda_2} = \exp\left[-m(K_{x,\lambda_1} - K_{x,\lambda_2})W\right]. \tag{7}$$

The absorption coefficients K_{x,λ_1} and K_{x,λ_2} are evaluated for Lorentz line-shape as

$$K_x = \frac{S\,\alpha\,\lambda_1^2\,\lambda_2^2}{\pi\left[(\lambda_1-\lambda_2)^2 + \alpha^2\lambda_1^2\lambda_2^2\right]} \text{ (molecule cm}^{-2})^{-1}, \tag{8}$$

where S is the line strength (cm^{-1}/molecule cm^{-2}), λ_1 is the wavelength at the centre of the line (cm), λ_2 is the wavelength in the atmospheric window region, where there is negligible absorption by the molecule.

The absorption features of NO_2, N_2O, NO and H_2O, and their respective absorption coefficients used in present study, are given in Table 1.

Thus by measuring I_{λ_1} and I_{λ_2}, the integrated columns of X (NO_2, N_2O, NO and H_2O) can be evaluated.

Table 1. Absorption features of NO_2, N_2O, NO and H_2O, and their respective absorption coefficients.

Molecule	Line position		Absorption coefficients K (molecule^{-1} cm^2)
	λ_1 (μm)	λ_2 (μm)	
NO_2	6 184	6 183	1.150×10^{-16}
	6 232	6 231	$1\ 165 \times 10^{-16}$
N_2O	8.560	8 559	$1\ 814 \times 10^{-19}$
	8 486	8 485	1.778×10^{-19}
NO	5 770	5 769	4.308×10^{-17}
	5 415	5 414	$4\ 250 \times 10^{-17}$
H_2O	6 500	6 499	$1\ 186 \times 10^{-23}$

3. Experimental details

A block diagram of the experimental set-up, controlled by a Sun follower, is shown in Figure 1.

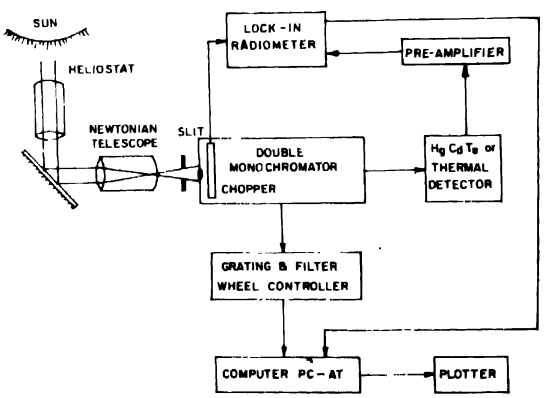


Figure 1. Solar infrared spectroradiometer.

The solar infrared spectroradiometer consists of double monochromators through which the solar radiations fall on HgCdTe detector which has a spectral response between 1 to 15 μm. While tracking the sun, the infrared spectroradiometer measures the transmitted solar intensity in wavelength interval of 0.001 μm to retrieve NO_2, N_2O, NO and H_2O integrated columns, using their respective selected absorption features. The overall spectral region from 1 to 15 μm is divided into smaller overlapping wavelength intervals using

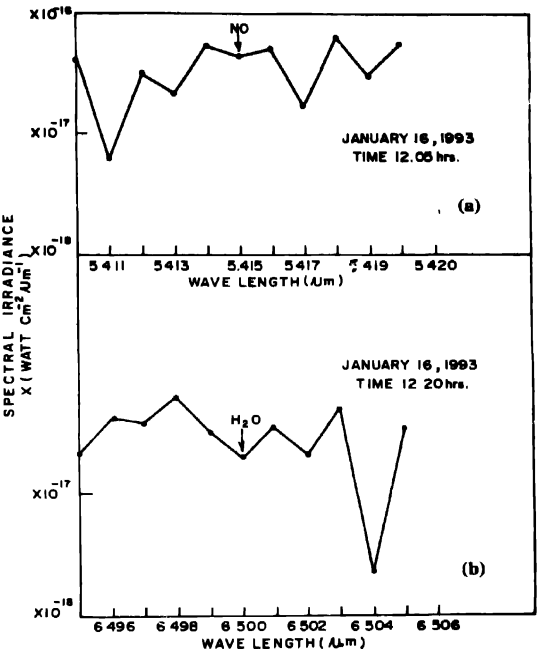
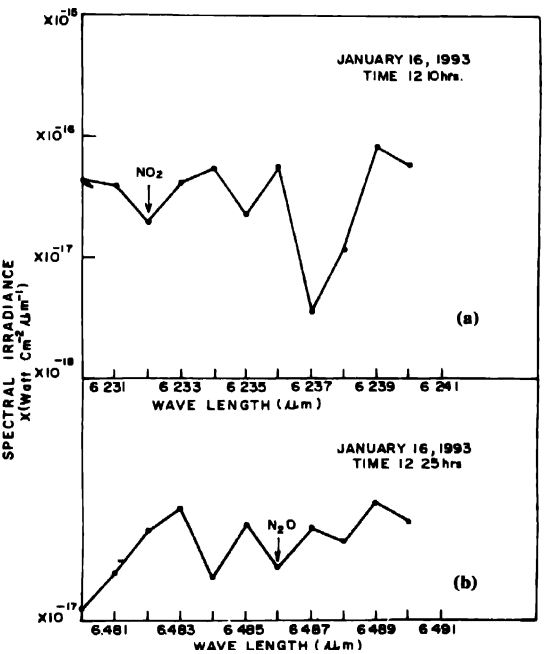


Figure 2. Absorption spectra containing absorption feature of (a) NO, (b) H_2O.



optical grating, which reduces the sampling rate, maximises detected energy and improves the signal to noise ratio of the spectra. The signal to noise ratio of the instrument is about 1000 and spectral resolution is comparable to line-width of the spectra. The line intensities have an uncertainty less than 10% and assigned values of uncertainties in spectral irradiance is estimated to be 8%. The stray light level is less than 0.1% for most wavelengths with a maximum error of 3%. The infrared spectroradiometer is controlled by a computer which accommodates a large dynamic range of the data values, displays and plots the measured absorption spectra and stores the data on floppy disk. The typical spectra of NO_2, N_2O, NO and H_2O are shown in Figures 2 and 3. The percentage absorption by NO_2, N_2O, NO and H_2O in the present spectra are approximately 49%, 54%, 12% and 47% respectively

The integrated column of X has been calculated using eq. (7) by selecting wavelength λ_1, the absorption line of the molecule and wavelength λ_2 in the atmospheric window region where there is negligible absorption by the molecule.

4. Results and discussion

NO_2 :

The NO_2 absorption feature at 6 184 μm and 6.232 μm are used for determination of integrated column of NO_2 during the months of May, June and July, 1992 and November, December 1992 and January 1993 respectively This region also contains absorption lines due to atmospheric water vapour, methane and solar CO lines. But high resolution solar spectroradiometer spectra identify this line with negligible interference.

The NO_2 integrated columns for the months of May, June and July 1992 (summer), vary from 3.290×10^{15} molecules cm^{-2} to 7.642×10^{15} molecules cm^{-2} with an average value of 5.255×10^{15} molecules cm^{-2} and for the months of November, December 1992 and January 1993 (winter) vary from 1.792×10^{15} molecules cm^{-2} to 7.562×10^{15} molecules cm^{-2} with an average value of 4.211×10^{15} molecules cm^{-2}.

Bhonde *et al* [14] measured NO_2 during May, June 1988 and February 1989 from zenith sky observations in visible region from the ground at Pune (18°32' N, 73°51' E) and found that NO_2 vary from 6.0×10^{15} molecules cm^{-2} to 13.0×10^{15} molecules cm^{-2} while Lal *et al* [15] measured NO_2 during December 1989 and January 1990 using ground based visible absorption spectrometry at Ahmadabad (23°N, 72°E) and found that NO_2 vary from 0.5×10^{15} molecules cm^{-2} to 2.8×10^{15} molecules cm^{-2}.

It can be seen that the summer months values of NO_2 reported by Bhonde *et al* [14] are higher and winter month values of NO_2 reported by Lal *et al* [15] are lower than the corresponding values of NO_2 presented in this paper. The minimum integrated column observed during winter period and maximum during summer period are in agreement with the reported measurements. But, it should be remembered that the values of Bhonde *et al* and Lal *et al* represent stratospheric NO_2 column.

N_2O :

The N_2O absorption feature at 8.560 μm present in the solar spectra recorded during May, June and July 1992 and absorption features at 8.486 μm recorded during November, December 1992 and January 1993, were used to determine N_2O column abundance.

The N_2O integrated column for the months of May, June and July 1992 (summer) vary from, 4.878×10^{18} molecules cm^{-2} to 5.620×10^{18} molecules cm^{-2} with an average value of 5.228×10^{18} molecules cm^{-2} and for the months of November, December 1992 and January 1993 (winter) vary from 4.653×10^{18} molecules cm^{-2} to 5.579×10^{18} molecules cm^{-2} with an average value of 5.21×10^{18} molecules cm^{-2}.

NO :

The well-isolated nitric oxide line at 5.770 μm present in the solar spectra recorded during May, June and July 1992 and line at 5.415 μm recorded during November, december 1992 and January 1993 were used to determine NO column abundance. The NO column density for the months of May, June and July 1992 (summer) vary from 3.831×10^{15} molecules cm^{-2} to 6.141×10^{15} molecules cm^{-2} with an average value of 4.980×10^{15} molecules cm^{-2} and for the months of November, December 1992 and January 1993 (winter) vary from 1.143×10^{15} molecules cm^{-2} to 5.263×10^{15} molecules cm^{-2} with an average value of 2.819×10^{15} molecules cm^{-2}.

H_2O :

The H_2O absorption feature at 6.500 μm is used for the determination of integrated column of H_2O during the months of May, June, July, November, December 1992 and January 1993

The H_2O integrated columns for the months of May, June and July 1992 (summer) vary from 0.927×10^{23} molecules cm^{-2} to 1.971×10^{23} molecules cm^{-2} with an average value of 1.408×10^{23} molecules cm^{-2} and for the months of November, December 1992 and January 1993 (winter) vary from 0.585×10^{23} molecules cm^{-2} to 1.189×10^{23} molecules cm^{-2} with an average value of 0.764×10^{23} molecules cm^{-2}.

The line parameters, the line strength and the Lorentz half-width for determination of NO_2, N_2O, NO and H_2O are taken from the HITRAN Molecular Database [13]. The time profiles of NO_2, N_2O, NO and H_2O for May, June and July 1992 and November, December 1992 and January 1993 are presented in Figure 4. The ozone Dobson data obtained from IMD for the same period and site is also ploted in this figure.

It is evident from the above results that NO_2 shows seasonal variation with higher values in summer than in winter. The average value of integrated column in summer is larger by a factor of 1.248 as compared to integrated columns in winter months. The average value of column density of N_2O in summer and in winter months are almost equal

and having only a slight seasonal dependence. The behaviour of integrated column of NO is similar to that of NO_2. The average value of integrated column of NO in summer months is larger by a factor of 1.766 as compared to integrated column in winter months.

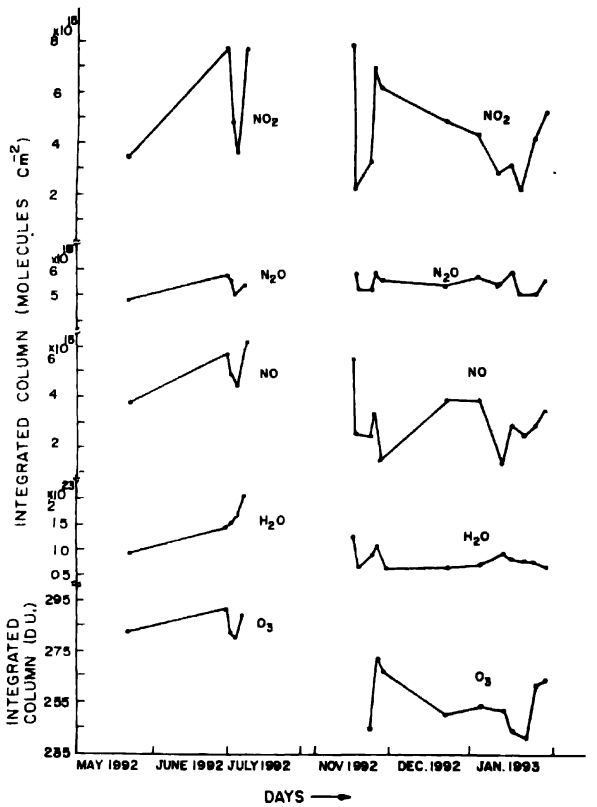


Figure 4. Integrated column of NO_2, N_2O, NO, H_2O and O_3 in May, June, July, November, December 1992 and January 1993.

5. Conclusion

We have measured atmospheric emissions in the infrared region from the ground. From these measurements, integrated columns of NO_2, N_2O and NO have been determined.

Seasonal fluctuations in the integrated columns of NO_2 and NO have been observed. The summer months are characterised by rather high values of integrated columns of NO_2 and NO with average values 5.255×10^{15} molecules cm^{-2} and 4.980×10^{15} molecules cm^{-2}, respectively. In winter, the average values of integrated column of NO_2 and NO drop to 4.211×10^{15} molecules cm^{-2} and 2.819×10^{15} molecules cm^{-2}, respectively. The average values of integrated columns of N_2O in summer and winter months are almost equal.

Ozone distribution is found to be most sensitive to variation in integrated columns of NO_2, NO and N_2O and less sensitive to the variations in the integrated column of water vapour.

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